THE ESTERIFICATION OF BENZOIC ACID BY ISOMERIC BUTYL MERCAPTANS

DISSERTATION

Submitted to the Board of University Studies of The Johns Hopkins University in Conformity with the Requirements for the Degree of Doctor of Philosophy.

BY

JOHN WILLARD KIMBALL.

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HISTORICAL.

The influence of isomerism on the rates and limits of esterification of alcohols has been carefully studied by Menschutkin,[1] who found that the limit for primary alcohols, whether normal or iso-, was practically the same; while that for secondary alcohols was much lower. The limit for tertiary alcohols, he found to be still lower but the results in this case were not the real limits since a part of the alcohol reacted in another way, decomposing into the unsaturated hydrocarbon and water.

With acetic acid Menschutkin[1] found the following limits for the isomeric butyl alcohols: normal 67.30%, iso- 67.38%, secondary 59.28%, tertiary 7.10%. The limits were reached in 120 hours at 154 degrees.

Reid,[2] studying the mechanism of the reaction in esterification, employed mercaptans instead of alcohols and showed that the reaction

$$C_6H_5COOH + HSC_2H_5 \rightleftarrows C_6H_5COSC_2H_5 + H_2O.$$

in this case reaches a well defined limit as in the case of the oxygen alcohols.

Pratt and Reid[3] then took up this work, using benzoic acid with methyl, ethyl and propyl mercaptans and accurately determined the limits of these systems. These limits with mercaptans were found to be much lower than those found by Berthelot and St. Gilles[4] and by Menschutkin[5] with alcohols but the relations between the limits in the two series are much the same.

As pointed out by Pratt and Reid,[3] it is much more dif-

1 Ber **11,** 1507, 2117, 2148, (1878); Ann. (Liebig) **195,** 334 (1879); **197,** 193 (1879); Ann. Chim. Phys. (5) **20,** 289 (1880).
2 Am. Chem. Jr. **43,** 489 (1910).
3 J. Am. Chem. Soc. **37,** 1934 (1915).
4 Ann. Chim. Phys. (3) **65,** 385 (1862); **66,** 5 (1862); **68,** 225 (1863).
5 Ber. **10,** 1728 (1877); **11,** 1507 (1878).

ficult to get concordant results with mercaptans than with alcohols, since the mercaptans must be eliminated before titration of the unesterified acid. The use in individual experiments of varying amounts of mercaptan and acid, instead of the identical and equivalent amounts of alcohol and acid such as have commonly been used, also increases the difficulty.

MATERIALS.

Benzoic Acid.—The benzoic acid used was a well known firm's best grade.

Mercaptans.—The normal mercaptan[6] was prepared from normal butyl bromide and potassium hydrosulphide. The mercaptan obtained was dried over calcium chloride, fractionated several times and the fraction boiling 97°-98° used in the work.

The isobutyl mercaptan used was a standard commercial product.

The secondary butyl mercaptan[7] was prepared from secondary butyl bromide and potassium hydrosulphide. The mercaptan was dried over calcium chloride, fractionated several times, and the fraction boiling 83°-84° used.

An effort was made to prepare the tertiary mercaptan according to the method of Dobbin[8] except that tertiary butyl bromide was used instead of the iodide but only traces of the desired mercaptan were obtained. On account of the difficulties involved this preparation was abandoned.

Normal, Iso-, Secondary, and Tertiary Butyl Thiolbenzoates.—The thiol esters were made by alkylating thiol benzoic acid, prepared according to Kym's[9] general directions. The acid was, however, purified by dissolving the

6 Grabowsky & Saytzeff, Ann. (Lieb) **171,** 251 (1874).
7 Reyman, Ber. **7,** 1287 (1874).
8 J. Chem. Soc. **57,** 640 (1890).
9 Ber. **32,** 3533, (1899).

potassium salt in water, filtering and liberating the acid with hydrochloric acid. After settling the oily acid was separated and the aqueous solution extracted with ether. On evaporation of the ether the acid was ready for use. The potassium salt of the purified thiol benzoic acid was treated, according to the general directions of Wheeler,[10] with the butyl bromide of which the ester was desired. The esters so obtained were carefully fractionated in a partial vacuum. The boiling points and densities of these butyl thiol benzoates are given in the following table:

Normal	160° at 23 mm.	1.0514 25/25
Iso-	150° at 20 mm.	1.0457 25/25
Secondary	151° at 23 mm.	1.0488 25/25
Tertiary	110° at 28 mm.	1.0468 25/25

The normal and iso- esters were reddish in color when first prepared but on standing for several months the color faded to a light pink. The secondary ester faded from yellow to nearly colorless while the tertiary faded from a very light yellow to colorless. It seems probable that the color is due to some slight impurity.

Water.—Conductivity water was used.

APPARATUS.

The furnace used was that described by Pratt and Reid.[11]

The standard solutions of barium hydroxide and hydrochloric acid were kept in the apparatus used by them. These solutions were approximately 0.1 normal and were standardized frequently by titration against benzoic acid.

10 Am. Chem. J. **24**, 69 (1900).
11 Loc. cit.

PROCEDURE.

Hard glass tubes about 3.5—4.5 mm. inside diameter by 75 mm. long, closed at one end, were boiled for six hours in dilute hydrochloric acid, one hour in distilled water and thoroughly dried.

Acid Series.—Each tube was weighed, partially filled with benzoic acid, drawn out to a narrow neck and weighed again. The mercaptan was then introduced, the tube sealed and finally the tube and tip weighed together.

Ester Series.—Each tube was weighed, partially filled with ester, drawn out and weighed again. Two or three drops of water were then added and the tube and tip weighed after sealing.

The tubes were then heated in the furnace for the length of time desired at 200 degrees.

To analyze, the tubes were broken into 120 c. c. Erlenmeyer flasks through a funnel with a short wide stem and the contents dissolved in 20-25 c. c. of alcohol, recently distilled from caustic potash.

The mercaptan was then blown off by passing a current of CO_2-free air through the solution heated to 50 degrees. In preliminary experiments with known amounts of benzoic acid and mercaptan, it was found necessary to pass air through the solutions twenty-five minutes to remove normal mercaptan, twenty minutes to remove the iso-, and fifteen to remove the secondary, and this procedure was followed.

The benzoic acid present was then titrated with the standard barium hydroxide, using phenolphthalein as indicator.

EXPERIMENTAL.

Since[12] according to the usual reasoning in the consideration of reversible reactions, the amount of ester

12 Pratt & Reid, loc. cit.

formed in unit time is equal to (Benzoic acid) (Mercaptan) K and the amount of ester decomposed in the same time is equal to (Ester) (Water) K′ (the expressions in parentheses represent concentrations) and since at equilibrium these opposing velocities are equal, we have:

$$\frac{\text{(Benzoic acid) (Mercaptan)}}{\text{(Ester) (Water)}} = \frac{K'}{K} = r \qquad (1)$$

Now for equivalent concentrations of acid and mercaptan at equilibrium

$$\frac{\text{Amount of mixture unesterified}}{\text{Amount of mixture esterified}} = \frac{\sqrt{K'}}{\sqrt{K}} = \frac{\sqrt{r}}{1}, \text{ or}$$

$$\frac{\text{Amount of mixture esterified}}{1} = \frac{100}{\sqrt{r} + 1}.$$

In percentage this becomes:

$$\text{Per cent. of mixture esterified at limit} = \frac{100}{\sqrt{r} + 1}. \qquad (2)$$

In the first experiments the tubes used had an internal diameter of about 4.5 mm. and the rate of esterification in them seems to have been quite different from that in the smaller tubes (3.5 mm. inside diameter) used later as will be seen from the following tables, though Berthelot and St. Gilles[13] state that is is permissible to vary the volume of the unfilled portion considerably without modifying sensibly either the rate or limit of the reaction. In their work alcohols and acetic acid were used which do not differ greatly in volatility, but in the present work there is much difference in volatility between benzoic acid and the butyl mercaptans.

In the earlier experiments it was found in the ester-water series that an excess of ester over water gave place to some decomposition which yielded acid, since the results gave too low values for the limit. Samples of esters heated alone in the ordinary tubes to 200 degrees for several days gave considerable acid, showing that the ester-water results could not be relied upon, at least in the case of an excess of ester over water.

13 Ann. Chim. Phys. (3) **66,** 50 (1862).

Later experiments using an excess of water were run in the smaller tubes and here results were not satisfactory, since equilibrium was not reached in the time allowed due to the nonmiscibility of ester in water and to the small surface of contact.

Tubes containing acid and mercaptan and others containing ester and water in about the usual amounts were heated to 200 degrees in a sulphuric acid bath so that the conditions obtaining in the tubes at that temperature could be observed. It was found that, while the acid and mercaptan formed a perfectly homogeneous solution at that temperature, the ester and water still remained in two distinct layers and showed no tendency to mix, separating rapidly after being shaken together. This undoubtedly shows why the esterification proceeds regularly and comparatively rapidly from the acid-mercaptan end, while the mixtures of esters and water are slow to react and yield irregular results.

In tabulating results the data involved are arranged as follows according to the plan adopted by Pratt and Reid:[14]

a. Acid or ester in grams.
b. Acid or ester in millimols.
c. Mercaptan or water in grams.
d. Mercaptan or water in millimols.
e. Cubic centimeters of alkali required for titration.
f. Millimols of acid present calculated from e. In ester series this equals mercaptan.
g. Millimols of mercaptan remaining (in acid series).
h. Millimols of ester remaining (in ester series).
k. Millimols of water remaining (in ester series).
m. Millimols of ester equals water (in acid series).
%. Percentage esterification. This is calculated by the formula deduced above for equivalent concentrations of acid and mercaptan or ester and water, r being calculated from (1) and substituted in (2).

In the acid series, the amount of ester = water (m) is found by subtracting the acid remaining (f) from the

14 Loc. cit.

original acid (b). The millimols of mercaptan remaining (g) is obtained by subtracting the amount of ester (m) from (d) the mercaptan originally present.

In the ester series, the amount of ester remaining (h) is obtained by subtracting the acid found (f) from the original ester present (b). The water remaining (k) is obtained by subtracting the acid present (f) from (d) the original amount of water present.

Bracket results are not used in calculating the limits.

Tables A-E inclusive were run in the tubes having the larger diameter, and tables F-K in the smaller.

TABLES OF RESULTS.

TABLE A. 24 HOURS AT 200°

C_4H_7COOH + n-C_4H_9SH.

b.	1.6837	1.8623	1.9262
d.	1.1061	1.0783	0.8043
f.	1.5210	1.6761	1.7560
g.	0.9434	0.8921	0.6341
m.	0.1627	0.1862	0.1702
$\sqrt{r}$.	7.3624	6.5672	7.8050
%.	11.96	(13.21)	11.36

Average, 11.66%

C_4H_7COOH + iso-C_4H_9SH.

b.	1.9549	2.4359	1.8443
d.	0.8798	1.4866	0.8997
f.	1.8185	2.2775	1.7242
g.	0.7434	1.3282	0.7796
m.	0.1364	0.1584	0.1201
$\sqrt{r}$.	8.5305	10.980	9.6536
%.	10.49	8.55	9.39

Average, 9.48%

C_4H_7COOH + sec-C_4H_9SH.

b.	1.8074	1.7009	1.9836
d.	0.9885	1.1150	0.8198
f.	1.6961	1.5773	1.8739
g.	0.8772	0.9914	0.7101
m.	0.1113	0.1236	0.1097
$\sqrt{r}$.	10.949	10.109	10.515
%.	8.37	9.00	8.68

Average, 8.68%.

TABLE B. 48 HOURS AT 200°.

C_4H_5COOH + n-C_4H_9SH.

b.	1.0160	1.2356	1.3576
d.	1.4034	1.5321	1.8305
f.	0.8562	1.0521	1.1528
g.	1.2436	1.3486	1.6257
m.	0.1598	0.1835	0.2048
V r.	6.4573	6.4956	6.6844
%.	13.41	13.34	13.02
		Average,	13.26%

C_4H_5COOH + iso-C_4H_9SH.

b.	1.5494	1.1651	0.8882
d.	1.2902	0.8687	1.3113
f.	1.3605	1.0494	0.7546
g.	1.1013	0.7630	1.1777
m.	0.1889	0.1157	0.1336
V r.	6.4799	7.6826	7.0553
%.	13.37	11.52	12.42
		Average,	12.44%.

C_4H_5COOH + sec-C_4H_9SH.

b.	1.2413	1.0242	1.0373	0.8955
d.	1.1271	1.5676	1.2514	0.9485
f.	1.1310	0.9143	0.9387	0.8127
g.	1.0168	1.4577	1.1528	0.8657
m.	0.1103	0.1099	0.0986	0.0828
V r.	9.7322	10.666	10.550	10.130
%.	9.32	8.57	8.66	8.98
			Average,	8.88%

TABLE C. 96 HOURS AT 200°.

C_6H_5COOH + n-C_4H_9SH.

b.	1.4601	1.0381	1.2093
d.	1.6608	1.3812	0.8398
f.	1.2707	0.8834	1.0811
g.	1.4714	1.2265	0.7116
m.	0.1894	0.1547	0.1282
Vr.	7.2240	6.7440	6.8479
%.	12.19	12.91	12.76

Average, 12.62%

C_6H_5COOH + iso-C_4H_9SH.

b.	1.2609	1.0971	0.9914
d.	1.5055	1.3590	1.7118
f.	1.0839	0.9605	0.8399
g.	1.3285	1.2224	1.5603
m.	0.1770	0.1366	0.1515
Vr.	6.7793	7.9325	7.5562
%.	12.85	11.20	11.69

Average, 11.91%

C_6H_5COOH + sec-C_4H_9SH.

b.	1.0496	0.9488	1.2437	0.8611
d.	1.2104	1.6153	1.0351	1.4700
f.	0.9542	0.8526	1.1555	0.7691
g.	1.1150	1.5191	0.9469	1.3780
m.	0.0954	0.0962	0.0882	0.0920
Vr.	10.811	11.830	11.860	11.203
%.	8.47	7.79	7.78	8.20

Average, 8.06%.

TABLE D. 192 HOURS AT 200°.

$C_6H_5COOH + n\text{-}C_4H_9SH.$

b	1.7960	1.9123	2.0197	2.1114	1.8779
d.	1.9880	1.5498	1.2603	1.6785	1.2625
f.	1.5709	1.6952	1.8140	1.8784	1.6770
g.	1.7629	1.3327	1.0546	1.4455	1.0616
m.	0.2251	0.2171	0.2057	0.2330	0.2009
√r.	7.3930	6.9234	6.7242	7.0722	6.6420
%.	(11.91)	12.62	12.95	12.39	13.09

Average, 12.76%.

$n\text{-}C_6H_5COSC_4H_9 + H_2O.$

b.	1.5692	1.5712	1.8220	1.3297	1.7535
d.	2.2480	1.7651	1.6763	0.8992	1.1878
f.	1.4848	1.4249	1.5238	0.8979	1.1764
h.	0.0844	0.1563	0.2982	0.4318	0.5771
k.	0.7632	0.3402	0.1525	0.0013	0.0114
√r.	5.8534	6.3860	7.1431		14.504
%.	14.59	13.54	(12.28)		(8.12)

Average, 14.06%

$C_6H_5COOH + iso\text{-}C_4H_9SH.$

b.	2.3867	2.0590	2.4883	2.3515	2.0180
d.	1.5177	1.5365	1.5698	1.4189	1.6807
f.	2.1478	1.8321	2.2185	2.1106	1.7732
g.	1.2788	1.3096	1.3000	1.1780	1.4359
m.	0.2389	0.2269	0.2698	0.2409	0.2448
√r.	6.9368	6.8268	6.2971	6.5454	6.5183
%.	12.60	12.78	13.73	13.25	13.30

Average, 13.15%

iso-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.5548	1.4919	1.6124	1.7711	1.6887
d.	0.9769	1.2878	0.9214	0.9936	0.7882
f_1	1.0594	1.1972	0.9288	1.0113	0.8018
h.	0.4954	0.2947	0.6863	0.7598	0.8869
k.		0.0906			
V r.		7.3326			
%.		(12.00)			

C_6H_5COOH + sec-C_4H_9SH.

b.	1.9484	2.0549	2.2958	2.1417	2.0754
d.	1.6475	1.4089	1.6075	1.7562	1.3945
f.	1.8095	1.9147	2.1287	1.9709	1.9365
g.	1.5086	1.2687	1.4404	1.5854	1.2556
m.	0.1389	0.1402	0.1671	0.1708	0.1389
V r.	11.90	11.12	10.479	10.343	11.226
%.	7.76	8.25	8.71	8.82	8.18

Average, 8.34%

sec-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.4806	2.0517	1.6923	1.4631	1.7123
d.	1.3100	2.7032	1.4376	1.2878	1.9705
f.	1.2136	1.9455	1.3723	1.2208	1.5873
h.	0.2670	0.1062	0.3200	0.2423	0.1250
k.	0.0964	0.7577	0.0653	0.0670	0.3832
V r.	7.5645	6.8585	9.4950	9.5818	7.2524
%.	(11.67)	12.72	(9.75)	(9.45)	12.12

Average, 12.42%

tert-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.6320	1.3179	1.3951	1.2113	1.3014
d.	1.3599	2.2425	2.0871	1.6375	1.5375
f.	0.7238	0.8118	0.8372	0.7755	0.6857
h.	0.9082	0.5061	0.5579	0.4358	0.6157
k.	0.6361	1.4307	1.2499	0.8620	0.8518
V r.	0.9501	0.9542	1.0025	1.2653	0.9499
%.	51.28	51.17	49.94	44.14	51.28

Average, 49.56%

TABLE E. 288 HOURS AT 200°.

C_6H_5COOH + n-C_4H_9SH.

b.	1.9435	1.9820	1.8886	2.1827	2.4236
d.	1.4300	1.5864	1.8494	1.6663	1.0528
f.	1.7175	1.7508	1.6481	1.9374	2.1933
g.	1.2040	1.3552	1.6089	1.4210	0.8225
m.	0.2260	0.2312	0.2405	0.2453	0.2303
√r.	6.3658	6.6624	6.7705	6.7640	5.8321
%.	13.58	13.05	12.87	12.88	14.64

Average, 13.40%

n-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.7139	1.6686	1.5455	1.8225	1.8926	1.6181	1.8308
d.	1.4099	1.2267	1.2822	1.0380	1.9872	1.7207	2.1537
f	1.3345	1.1913	1.2030	1.0516	1.6625	1.4264	1.6616
h.	0.3794	0.4773	0.3425	0.7709	0.2301	0.1917	0.1692
k.	0.0754	0.0354	0.0792		0.3247	0.2943	0.4921
√r.	7.8913	9.1513	7.2983		6.0823	6.0055	5.7585
%.	(11.25)	(9.76)	(12.33)		14.12	14.27	14.79

Average, 14.39%

C_6H_5COOH + iso-C_4H_9SH.

b.	2.3318	1.9484	2.1204	2.1991	2.0623
d.	1.7772	1.6519	1.6830	1.6231	1.6619
f.	2.0545	1.6977	1.8527	1.9320	1.8076
g.	1.4999	1.4012	1.4153	1.3560	1.4072
m.	0.2773	0.2507	0.2677	0.2671	0.2547
√r.	6.3304	6.1519	6.0464	6.0570	6.2617
%.	13.64	13.92	14.19	14.17	13.77

Average, 13.94%

iso-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.9564	1.7721	1.8859	2.0594	1.5486	1.5625	1.6675
d.	1.1768	1.3932	0.8104	2.0149	2.1592	2.4257	2.1925
f.	1.1687	1.3264	0.8281	1.7680	1.4300	1.4625	1.5310
h.	0.7877	0.4457	1.0578	0.2914	0.1186	0.1000	0.1365
k.	0.0081	0.0668		0.2469	0.7292	0.9632	0.6615
V r.	14.631	7.688		6.5887	4.8646	4.7122	5.0941
%.	(6.40)	(11.51)		(13.18)	17.05	17.51	16.41

Average, 16.99%

C_6H_5COOH + sec-C_4H_9SH.

b.	1.5256	2.0172	2.0500	1.3191	1.5289
d.	1.5765	1.3579	2.0202	1.8427	2.0579
f.	1.3931	1.8626	1.8743	1.1850	1.3877
g.	1.4440	1.2033	1.8445	1.7086	1.9167
m.	0.1325	0.1546	0.1757	0.1341	0.1412
V r.	10.704	9.6838	10.582	10.603	11.550
%.	8.54	9.36	8.63	8.62	7.97

Average, 8.62%

sec-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.6392	1.4986	1.4718	1.6011	1.8272
d.	1.8928	2.0815	2.0149	1.5320	1.8206
f.	1.5220	1.4165	1.3922	1.4059	1.6337
h.	0.1172	0.0821	0.0796	0.1954	0.1935
k.	0.3708	0.6650	0.6227	0.1263	0.1869
V r.	7.3009	6.0623	6.2533	8.9480	8.5906
%.	12.05	14.16	13.78	(10.05)	(10.43)

Average, 13.33%

tert-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.4301	1.4445	1.4214	1.3189	1.4348
d.	1.8595	1.8262	1.7596	1.4321	1.4709
f.	0.8209	0.8317	0.8272	0.7200	0.7371
h.	0.6092	0.6128	0.5942	0.5989	0.6977
k.	1.0386	0.9945	0.9324	0.7121	0.7338
V r.	1.0321	1.0654	1.1113	1.1025	1.0302
%.	49.21	48.42	47.36	47.56	49.37

Average, 48.38%

TABLE F. 24 HOURS AT 200°.

C_6H_5COOH + n-C_4H_9SH.

b.	1.3806	1.5731	1.5420	1.3601	1.5707
d.	1.3745	1.4810	1.6220	1.4999	1.3967
f	1.2915	1.4491	1.4049	1.2582	1.4572
g.	1.2854	1.3570	1.4849	1.3880	1.2832
m.	0.0891	0.1240	0.1371	0.1119	0.1135
V r.	14.461	11.309	10.535	11.763	12.076
%.	(6.47)	8.12	8.67	7.84	7.65

Average, 8.08%

C_6H_5COOH + iso-C_4H_9SH.

b.	1.7222	1.6403	1.7943	1.9902	1.9402
d.	1.2780	1.2203	1.2092	1.2081	1.2414
f.	1.6220	1.5256	1.6634	1.8543	1.8292
g.	1.1778	1.1056	1.0783	1.0722	1.1303
m.	0.1002	0.1147	0.1309	0.1359	0.1111
V r.	13.794	11.322	10.231	10.375	12.942
%.	(6.76)	8.12	8.90	8.79	(7.17)

Average, 8.60%

C_6H_5COOH + sec-C_4H_9SH.

b.	1.4248	1.8132	1.8492	1.9959
d.	1.3424	1.6796	1.6142	1.4810
f.	1.3698	1.7129	1.7607	1.9093
g.	1.2874	1.5793	1.5257	1.3944
m.	0.0550	0.1003	0.0885	0.0866
V r.	24.145	16.399	18.520	18.841
%.	(3.98)	5.75	5.12	5.04

Average, 5.30%

TABLE G. 48 HOURS AT 200°.

C_6H_5COOH + n-C_4H_9SH.

b.	1.5084	1.5723	1.6370	1.5903	1.7435
d.	1.6574	1.3912	1.4422	1.3490	1.2259
f.	1.3644	1.3914	1.4464	1.4130	1.5751
g.	1.5134	1.2103	1.2516	1.1717	1.0575
m.	0.1440	0.1809	0.1906	0.1773	0.1684
V r.	9.9790	7.1737	7.0592	7.2571	7.6640
%.	(9.12)	12.23	12.41	12.11	(11.54)

Average, 12.25%

C_6H_5COOH + iso-C_4H_9SH.

b.	1.9525	2.2122	1.8042	1.6895
d.	1.1349	1.1216	1.0218	0.5580
f.	1.7976	2.0092	1.6346	1.5851
g.	0.9800	0.9186	0.8522	0.4536
m.	0.1549	0.2030	0.1696	0.1044
V r.	8.5700	6.6923	6.9586	8.1222
%.	(10.45)	13.00	12.56	(10.97)

Average, 12.78%

C_6H_5COOH + sec-C_4H_9SH.

b.	1.6354	1.8058	2.1303	1.7739	2.0401
d.	1.2459	1.2869	1.6009	1.4866	1.5043
f.	1.5535	1.7003	1.9858	1.6499	1.9165
g.	1.1640	1.1814	1.4564	1.3626	1.3807
m.	0.0819	0.1055	0.1445	0.1240	0.1236
V r.	16.419	13.434	11.778	12.092	13.149
%.	(5.74)	6.93	7.83	7.64	7.07

Average, 7.37%

TABLE H. 96 HOURS AT 200°.

C_6H_5COOH + n-C_4H_9SH.

b.	1.5502	1.7820	1.7845	1.9271	1.8451
d.	1.1416	1.2814	1.2081	1.1039	1.3091
f.	1.3779	1.5698	1.5869	1.7220	1.6391
g.	0.9693	1.0692	1.0105	0.8988	1.1031
m.	0.1723	0.2122	0.1976	0.2051	0.2060
V r.	6.7070	6.1049	6.4087	6.0655	6.5274
%.	12.98	14.07	13.50	14.15	13.28

Average, 13.75%

C_6H_5COOH + iso-C_4H_9SH.

b.	1.6591	1.7730	1.9730	1.8976	1.9041
d.	1.3690	1.4700	1.4345	1.4189	1.4866
f.	1.4617	1.5535	1.7418	1.6850	1.6814
g.	1.1716	1.2505	1.2033	1.2063	1.2639
m.	0.1974	0.2195	0.2312	0.2126	0.2227
V r.	6.6293	6.3466	6.2616	6.7061	6.5427
%.	13.11	13.61	13.77	12.98	13.26

Average, 13.38%

C_6H_5COOH + sec-C_4H_9SH.

b.	1.7444	1.8206	1.7460	2.0770	1.8394
d.	1.4777	1.3690	1.3346	1.3967	1.3623
f.	1.6166	1.6913	1.6175	1.9327	1.7147
g.	1.3499	1.2397	1.2061	1.2524	1.2376
m.	0.1278	0.1293	0.1285	0.1443	0.1247
$\sqrt{r}$.	11.559	11.208	10.870	10.782	11.692
%.	7.96	8.20	8.42	8.49	7.89

Average, 8.19%

TABLE I. 192 HOURS AT 200°.

C_6H_5COOH + n-C_4H_9SH.

b.	1.6870	1.9836	1.9623	2.0705	1.8025
d.	0.9874	1.2281	1.1072	1.0872	1.0750
f.	1.5094	1.7580	1.7445	1.8534	1.6085
g.	0.8098	1.0025	0.8894	0.8701	0.8810
m.	0.1776	0.2256	0.2178	0.2171	0.1940
$\sqrt{r}$.	6.2252	5.8846	5.7161	5.8496	6.1326
%.	13.84	14.52	14.89	14.60	14.02

Average, 14.37%

C_6H_5COOH + iso-C_4H_9SH.

b.	1.8083	2.1311	1.9222	1.8869	2.1393
d.	1.4688	1.3834	1.3823	1.2913	1.4411
f.	1.5977	1.8976	1.7021	1.6751	1.8994
g.	1.2582	1.1499	1.1622	1.0795	1.2012
m.	0.2106	0.2335	0.2201	0.2118	0.2399
$\sqrt{r}$.	6.7288	6.3233	6.3901	6.3488	6.2963
%.	12.94	13.66	13.53	13.61	13.71

Average, 13.50%

$C_6H_5COOH + sec\text{-}C_4H_9SH.$

b.	2.0860	1.8001	1.9197	1.9525	2.0639
d.	1.3268	1.4034	1.2348	1.3479	1.5898
f.	1.9417	1.6634	1.1832	1.7607	1.9093
g.	1.1825	1.2667	1.0983	1.1561	1.4352
m.	0.1443	0.1367	0.1365	0.1918	0.1546
V r.	10.493	10.619	10.252	7.4386	10.707
%.	8.70	8.61	8.89	(11.85)	8.54

Average, 8.70%

TABLE J. 288 HOURS AT 200°.

$C_6H_5COOH + n\text{-}C_4H_9SH.$

b.	1.6231	1.6075	1.5944	1.2994	1.5117
d.	1.7773	1.7429	1.5532	1.5931	1.5709
f.	1.3827	1.3628	1.3682	1.0920	1.2912
g.	1.5369	1.4982	1.3270	1.3857	1.3504
m.	0.2404	0.2447	0.2262	0.2074	0.2205
V r.	6.0630	5.8393	5.9568	5.9342	5.9887
%.	14.16	14.62	14.37	14.42	14.31

Average, 14.38%.

$n\text{-}C_6H_5COSC_4H_9 + H_2O.$

b.	1.5239	1.6026	1.5594	1.4425	1.4028
d.	3.4525	2.2702	2.9197	2.3535	2.0427
f.	1.0459	1.2704	1.1953	1.1590	1.1047
h.	0.4780	0.3322	0.3641	0.2835	0.2981
k.	2.4066	0.9998	1.7244	1.1945	0.9380
V r.	0.9513	2.2045	1.5084	1.9925	2.0892
%.	51.25	31.21	39.86	33.42	32.37

$C_6H_5COOH + iso\text{-}C_4H_9SH.$

b.	2.0311	1.8541	1.3527	1.7288	1.7280
d.	1.7706	1.9559	1.6009	1.6031	1.3490
f.	1.7712	1.5928	1.1482	1.5095	1.5194
g.	1.5107	1.6946	1.3964	1.3838	1.1404
m.	0.2599	0.2613	0.2045	0.2193	0.2086
V r.	6.2913	6.2846	6.1919	6.5904	6.3133
%.	13.72	13.73	13.90	13.18	13.67

Average, 13.64%

$iso\text{-}C_6H_5COSC_4H_9 + H_2O.$

b.	1.4821	1.5496	1.5923	1.6341	1.2957
d.	3.2805	3.6357	2.7143	3.5469	3.1417
f.	1.0069	0.9861	1.2433	1.1464	0.8140
h.	0.4752	0.5635	0.3490	0.4877	0.4817
k.	2.2736	2.6496	1.4710	2.4005	2.3277
V r.	0.9687	0.8108	1.7352	1.0596	0.7694
%.	50.80	55.00	36.56	48.55	56.50

$C_6H_5COOH + sec\text{-}C_4H_9SH.$

b.	1.3101	1.4871	1.5616	1.6010	1.7312
d.	1.5776	1.6785	1.6663	1.5665	1.7484
f.	1.1826	1.3492	1.4081	1.4579	1.5837
g.	1.4501	1.5406	1.5128	1.4234	1.6009
m.	0.1275	0.1379	0.1535	0.1431	0.1475
V r.	10.271	10.455	9.507	10.066	10.795
%.	8.87	8.73	9.51	9.04	8.48

Average, 8.92%

sec-$C_6H_5COSC_4H_9$ + H_2O.

b.		1.4811	1.5074	1.3261
d.		3.1917	4.0409	2.8475
f.		1.0468	0.9019	0.9272
h.		0.4343	0.6055	0.3989
k.		2.1449	3.1390	1.9203
V r.		1.0850	0.6543	1.0594
%.		47.96	60.40	48.50

tert-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.5115	1.7056	1.6454	1.4657
d.	3.8411	3.1195	3.5191	3.6746
f.	0.5687	0.6212	0.5976	0.5279
h.	0.9428	1.0844	1.0478	0.9378
k.	3.2724	2.4983	2.9215	3.1467
V r.	0.3237	0.3774	0.3416	0.3074
%	75.5	72.6	74.5	76.5

TABLE K. 28 DAYS AT 200°.

tert-$C_6H_5COSC_4H_9$ + H_2O.

b.	1.3678	1.4121	1.6289	1.5223	1.3920
d.	2.5311	2.7698	2.1259	1.9650	2.2647
f.	0.3197	0.3107	0.4458	0.4053	0.3323
h.	1.0481	1.1014	1.1831	1.1170	1.0597
k.	2.2114	2.4501	1.6801	1.5597	1.9324
V r.	0.2100	0.1888	0.3162	0.3070	0.2322
%.	82.6	84.1	76.0	76.5	81.2

DISCUSSION OF RESULTS.

From a study of the above data, it is seen that while the rate of esterification in the larger tubes is quite different from that in the smaller tubes, yet the limits are not very widely different. Since those in the larger tubes were done first and were in a way preliminary, the values obtained in the series run in the small tubes are taken as more nearly the true values.

Days	1	2	4	8	12
Normal	8.08%	12.25%	13.75%	14.37%	14.38%
Iso-	8.60%	12.78%	13.38%	13.50%	13.64%
Sec.	5.30%	7.37%	8.19%	8.70%	8.92%

Though the values of the limit from the ester-water end are not very reliable, it is indicated from the values in tables D and E that the limits above are nearly the true limits. This is also shown by the close agreement of the values in the last two columns shown above.

It is seen that both the rates and the limits of the normal and iso- mercaptans are nearly the same as was found to be the case with alcohols. Both these are primary mercaptans and the fact that one is a straight chain and the other a forked chain compound seems to make little difference. The secondary mercaptan however is seen to esterify slower and to reach a lower limit than the primary as was also found to be the case with alcohols.

The stability of the esters, as was shown by the work of Pratt and Reid, decreases with increasing molecular weight and it was found that in nearly all the tubes there were at least traces of hydrogen sulphide after heating to 200 degrees. The decomposition of the esters seems to take place more readily when little water is present and to give rise to the formation of an acid, since in tubes where there is an excess of ester over water the amount saponified as determined by titration goes below the limit.

It is also seen that the percentage saponification varies greatly with the relative amounts of water present, less

saponification taking place in cases with relatively large amounts of water. This is no doubt due to the immiscibility of ester and water at the temperature employed.

With the tertiary ester and water, little is shown except that this ester reacts differently from the others and gives rise to a different decomposition, since less acid was found after heating twenty-eight days than after heating twelve days.

CONCLUSIONS.

1. The rates and limits of esterification of benzoic acid by isomeric butyl mercaptans have been studied and the limits determined at 200 degrees.
2. The rates and limits for normal and iso- mercaptans were found to be nearly the same, but those for the secondary mercaptan much lower.
3. The limits found were much lower than those for the corresponding alcohols.
4. The saponification of the esters was found to be very irregular and unreliable on account of the immiscibility of ester and water and the decomposition of the esters.
5. The limits were found to be independent of the relative amounts of acid and mercaptan present.

BIOGRAPHY.

John Willard Kimball was born near Manhattan, Kansas, July 30, 1889. He received his early education in the district schools of that place and later removed to Riverside, California, where he completed his grammar school education and two years' work in the high school. He then removed to Moodus, Connecticut, and completed his secondary school education at the Connecticut Literary Institution, Suffield, Connecticut, in 1908. He entered Colby College in the fall of 1908 and was graduated in 1912 with the degree of Bachelor of Science. During the year 1912-1913 he was instructor in chemistry at Colby College. He entered Johns Hopkins University in the fall of 1913, taking chemistry as a major subject and Physical Chemistry and Applied Electricity as subordinate subjects. He held a University Scholarship during the year 1915-1916.